



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Tsutomu FUKUDA et al.

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For: METHOD FOR PRODUCING ALUMINUM TITANATE SINTERED
COMPACT

DECLARATION

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir :

I, Tsutomu FUKUDA, hereby declare:

1) That I am one of the inventors of the instant invention, and

2) That the experiments given below were carried out under my general direction and supervision.

Experiment 1

1. Purpose of Experiment

The purpose of the experiment is to confirm that a sintered body of aluminum titanate as defined in claim 5 of the present application with a molar ratio of Si to Mg of the raw material composition being in the range of Si:Mg = 0.9:1 to 1.1:1 exhibits greatly improved mechanical strength and resistance to thermal decomposition, and to show the difference between the sintered body of the present invention and the sintered body disclosed in Japanese Unexamined Patent Publication No. H04-280863.

2. Sample preparation method

(1) A sintered body of aluminum titanate was prepared by following the procedure of Example 1 in the

specification of this application. The Si:Mg molar ratio of the raw material composition used was 1.06:1. This sintered body is referred to as sample A.

(2) A sintered body of sample No. 3 shown in Fig. 4 of Japanese Unexamined Patent Publication No. H04-280863 was prepared by following the procedure of Example of Japanese Unexamined Patent Publication No. H04-280863. The Si:Mg molar ratio of the raw material composition used was 1.18:1. This sintered body is referred to as sample B.

(3) A sintered body was prepared by following the procedure of Example of Japanese Unexamined Patent Publication No. H04-280863, except that the amount of additive(s) of sample B was changed as shown in Table 1. The Si:Mg molar ratio of the raw material composition used was 0.84:1. This sintered body is referred to as sample C.

The raw material composition and the Si:Mg molar ratio of each sample are shown in Table 1.

Table 1

Samples	Raw material composition (part by weight)						Si:Mg molar ratio of the raw material composition
	Al ₂ TiO ₅	Al ₂ O ₃	TiO ₂	Alkali feldspar	Spinel	Sumecton SA	
A	-	56.1	43.9	4.0	6.0	-	1.06
B	90	-	5.0	-	-	5.0	1.18
C	90	-	5.0	-	2.0	5.0	0.84

3. Test method and test results

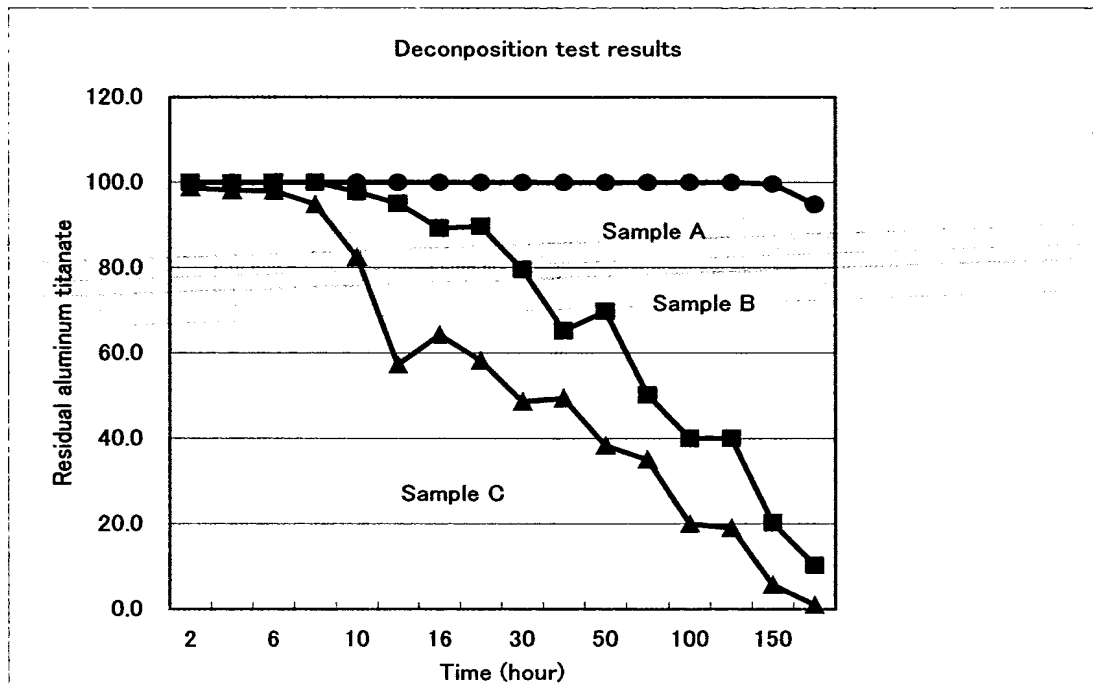
Three point bending strength and coefficient of thermal expansion were measured for the sintered body samples A to C according to the procedure of Examples 1 and 2 in the present specification. Further, as a test for resistance to thermal decomposition, the samples were maintained in air at 1000°C, and the change of residual aluminum titanate percentage over time was determined by following the procedure of Example 2.

Table 2 shows the measured three point bending strength and coefficient of thermal expansion of each sample.

The test results for the resistance to thermal decomposition are graphed in the following figure that shows the change of residual aluminum titanate percentage over time.

Table 2

Samples	Si/Mg molar ratio	Coefficient of thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$)	Three point bending strength (MPa)
A	1.06	1.1	85.7
B	1.18	1.0	3.4
C	0.84	1.3	10.3



4. Consideration

As is clear from the test results for sample A, the sintered body prepared from a raw material composition whose Si:Mg molar ratio was in the range of 0.9:1 to 1.1:1 exhibits extremely high mechanical strength and excellent resistance to thermal decomposition while maintaining a low coefficient of thermal expansion.

In contrast, sample B prepared from a raw material composition whose Si:Mg molar ratio was 1.18:1 and sample C prepared from a raw material composition whose Si:Mg molar ratio was 0.84:1 were significantly inferior to sample A in the strength and resistance to thermal decomposition.

These results show that a sintered body prepared using a raw material composition with a Si:Mg molar ratio in the range of 0.9:1 to 1.1:1 has an extremely high strength and excellent resistance to thermal decomposition compared to a sintered body prepared using a raw material composition whose Si:Mg molar ratio is less than 0.9:1 or higher than 1.1:1.

* * * * *

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: May 29, 2006

Masaaki Fukuda

Masaaki FUKUDA



VERIFICATION OF TRANSLATION

Re: JAPANESE PATENT APPLICATION NO.2002-126553

I, Keiko HOSOKAWA, of Kitahama TNK Building,
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hereby declare that I am the translator of the
document attached and certify that the following is
true translation to the best of my knowledge and
belief.

Signature of translator

Keiko Hosokawa
Keiko HOSOKAWA

Dated this 30th day of May, 2006



-1-

[Document Name] Specification

[Title of the Invention] PROCESS FOR PREPARING ALUMINUM-BASED TITANATE SINTERED BODY

[Claims]

5 [Claim 1] A process for preparing a sintered body of aluminum-based titanate, the process comprising sintering a formed product at a temperature of 1300 to 1700°C

 the formed product being prepared from a mixed
10 starting material comprising:

 100 parts by weight of a mixture comprising 40 to 50 mol% of TiO_2 and 60 to 50 mol% of Al_2O_3 ,

 1 to 10 parts by weight of an alkali feldspar represented by the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$ ($0 \leq x \leq 1$), and

15 1 to 10 parts by weight of at least one species selected from the group consisting of a Mg-containing oxide with spinel structure, MgCO_3 and MgO .

 [Claim 2] A process for preparing a sintered body of aluminum-based titanate according to claim 1, wherein
20 the alkali feldspar has such a composition that x in the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$ is in the range of $0.1 \leq x \leq 1$.

 [Claim 3] A sintered body of aluminum-based titanate obtained by a process according to Claim 1 or 2.

[Detailed Description of the Invention]

25 [0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a process for preparing a sintered body of aluminum-based titanate.

[0002]

5 [Prior Art]

Sintered bodies of aluminum titanate have a low coefficient of thermal expansion and high corrosion resistance. They are known as heat-resistant materials which exhibit low wettability with slag, high corrosion
10 resistance, high spalling resistance and other excellent properties when used as materials of, for example, containers, ladles, tapping spout, etc., for molten metals such as aluminum, aluminum alloy, ferroalloy and the like. However, the sintered bodies of aluminum titanate, whose
15 crystal grains constituting the sintered bodies are anisotropic, suffer the following disadvantages: displacement at the crystal grain boundaries are easily caused by stress due to the anisotropy of thermal expansion coefficient when the sintered bodies are heated
20 or cooled; consequently, micro cracks and apertures are formed which may lead to lowered mechanical strengths.

[0003]

Hence, conventional sintered bodies of aluminum-based titanate are insufficient in strengths, and cannot
25 exhibit desired durability particularly when used under

the conditions with high temperatures and heavy loads.

[0004]

In addition, aluminum titanate is unstable at a temperature of 1280°C or below. It tends to decompose
5 into TiO_2 and Al_2O_3 when it is used in a temperature range of about 800 to 1280°C, and therefore is unsuitable for continuous use in this temperature range.

[0005]

To improve the sinterability of aluminum-based
10 titanate and inhibit thermal decomposition, additives such as silicon dioxide and the like are mixed with starting materials prior to sintering. In this case, however, the refractoriness of the resulting sintered bodies tends to be lowered. For this reason, it has been
15 impossible to obtain a sintered body of aluminum-based titanate that is highly refractive and usable at a temperature of about 1400°C or higher, and also has high mechanical strengths.

[0006]

20 [Problems to Be Solved by the Invention]

A primary object of the present invention is to provide a sintered body of aluminum-based titanate having mechanical strengths improved to a practically usable level and capable of being stably used at high
25 temperatures while retaining their inherent properties,

i.e., low coefficient of thermal expansion and high corrosion resistance.

[0007]

[Means for Solving the Problems]

5 The inventors carried out intensive research to overcome the foregoing problems of the prior art. Consequently, the inventors found that, when a specific alkali feldspar and at least one species selected from the group consisting of a Mg-containing oxide with spinel
10 structure, MgCO_3 and MgO are admixed with a powdery material comprising titanium dioxide and aluminum and the resultant mixture is sintered, a sintered body of aluminum-based titanate with greatly improved mechanical strengths, resistance to thermal decomposition and high
15 refractoriness can be obtained without losing low thermal expansion inherent in aluminum-based titanate due to the synergistic effect of the Mg-containing component and alkali feldspar. The present invention was accomplished on the basis of this finding.

20 [0008]

 The present invention provides the process for preparing a sintered body of aluminum-based titanate described below.

 1. A process for preparing a sintered body of
25 aluminum-based titanate, the process comprising sintering

a formed product at a temperature of 1300 to 1700°C

the formed product being prepared from a mixed starting material comprising:

100 parts by weight of a mixture comprising 40 to
5 50 mol% of TiO_2 and 60 to 50 mol% of Al_2O_3 ,

1 to 10 parts by weight of an alkali feldspar represented by the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$ ($0 \leq x \leq 1$), and

1 to 10 parts by weight of at least one species selected from the group consisting of a Mg-containing
10 oxide with spinel structure, MgCO_3 and MgO .

2. A process for preparing a sintered body of aluminum-based titanate according to claim 1, wherein the alkali feldspar has such a composition that x in the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$ is in the range of $0.1 \leq x \leq 1$.

15 3. A sintered body of aluminum-based titanate obtained by a process according to Claim 1 or 2.

[0009]

[Mode for Carrying out the Invention]

The process for preparing a sintered body of
20 aluminum-based titanate of the invention is a process in which a composition prepared by blending a mixture comprising TiO_2 and Al_2O_3 with an alkali feldspar represented by the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$ ($0 \leq x \leq 1$) and at least one Mg-containing member selected from the group
25 consisting of a Mg-containing oxide having spinel

structure, MgCO_3 and MgO is used as a starting material; and a formed body prepared from this composition is sintered at a temperature of 1300 to 1700°C.

[0010]

5 TiO_2 and Al_2O_3 used as components in the starting materials are not limited insofar as they are substances from which aluminum-based titanate can be synthesized by sintering. Usually, they may be suitably selected from the materials used for producing various ceramics such as
10 alumina ceramics, titania ceramics, aluminum titanate ceramics and so on.

[0011]

The proportion of TiO_2 and Al_2O_3 in the mixture may be in a range of 40 to 50 mol% of TiO_2 and 60 to 50
15 mol% of Al_2O_3 , preferably 45 to 50 mol% of TiO_2 and 55 to 60 mol% of Al_2O_3 . In particular, adjusting the molar ratio of $\text{Al}_2\text{O}_3/\text{TiO}_2$ to 1 or higher within the mixing proportion mentioned above enables preventing coexistence of a liquid phase.

20 [0012]

The alkali feldspar used as an additive is represented by the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$, in which $0 \leq x \leq 1$. In particular, in the above-mentioned formula, it is preferable that x is in the range of $0.1 \leq x \leq 1$, and is
25 more preferable that x is in the range of $0.15 \leq x \leq 0.85$.

The alkali feldspar having such a value range of x has a low melting point, and thus is especially effective for promoting sintering of aluminum-based titanate.

[0013]

5 The amount of the alkali feldspar used is usually about 1 to 10 parts by weight, preferably about 3 to 4 parts by weight, per 100 parts by weight of the total amount of TiO_2 and Al_2O_3 .

[0014]

10 In the present invention, the Mg-containing oxide with spinel structure, MgCO_3 and MgO may be used singly or in combination of two or more kinds. Among these, examples of usable Mg-containing oxides with spinel structure include MgAl_2O_4 , MgTi_2O_4 and the like. Natural
15 minerals with spinel structure may be used as such oxides. Spinel oxides prepared by sintering a material comprising MgO and Al_2O_3 or a material comprising MgO and TiO_2 , etc. may be also used. Two or more different kinds of oxides with spinel structure may be used in combination.

20 [0015]

 At least one component selected from the group consisting of a Mg-containing oxide with spinel structure, MgCO_3 and MgO (hereinafter referred to as "Mg-containing component") may be used in an amount of about 1 to 10
25 parts by weight, preferably about 3 to 6 parts by weight,

per 100 parts by weight of the total amount of TiO_2 and Al_2O_3 .

[0016]

In the process of the present invention, the
5 molar ratio of Si in the alkali feldspar to Mg in the Mg-
containing component is preferably in the range of Si:Mg
= about 0.9 : 1.1, more preferably in the range of Si:Mg
= about 0.95 : 1.05.

[0017]

10 According to the process of the present invention,
a sintered body of aluminum-based titanate with high
mechanical strengths, high resistance to thermal
decomposition and high refractoriness can be obtained by
mixing the above-mentioned Mg-containing component and
15 alkali feldspar as additives with the mixture comprising
 TiO_2 and Al_2O_3 , forming this mixture into a desired shapes
and sintering the same.

[0018]

The mechanism how the sintered body with high
20 mechanical strength and high resistance to thermal
decomposition can be provided by the process of the
present invention is not fully clarified as yet, but is
presumed as follows.

[0019]

25 When aluminum-based titanate is synthesized by

sintering, Si atoms in the alkali feldspar dissolves into the crystal lattice and replaces part of Al atoms. Since Si has a smaller ion radius than Al, the bond length with neighboring oxygen atoms is shortened. The obtained
5 crystal will therefore have a smaller lattice constant than pure aluminum titanate. Accordingly, the resulting sintered body will have a stable crystal structure, improved mechanical strength and very high thermal stability, leading to greatly improved refractoriness.

10 [0020]

Further, the use of the Mg-containing component as an additive enables obtaining densified sintered body. Therefore, it is possible to form a sintered body having much higher mechanical strengths than pure aluminum
15 titanate.

[0021]

According to the process of the present invention, since the alkali feldspar and the Mg-containing component capable of attaining such effects are used as additives in
20 combination, it is presumed that Si contained in the alkali feldspar and Mg contained in the Mg-containing component replace mainly the Al sites in aluminum-based titanate. On the other hand, when each of these components is added singly, the Al sites, which originally keep their
25 electrical charge balance by being trivalent, are replaced

by either a divalent (Mg) or tetravalent (Si) element and thus the resulting sintered body needs to keep electrical balance. Therefore, in case where Mg is added, to keep the electrical charge balance, oxygen would be ejected from
5 the system to cause oxygen deficient in the sintered body. In case of adding tetravalent Si, which is inherently tetravalent, is assumedly reduced to be trivalent to keep the electrical charge balance. In the present invention, presumably, the electrical charge balance can be kept by
10 adding the alkali feldspar and Mg-containing component in combination because Mg has a charge number smaller than Al by 1 and Si has a charge number larger than Al by 1, whereby these elements can dissolve into the sintered body without affecting the other elements constituting the
15 sintered body. Particularly, when the amounts of the two additives are approximately equimolar, it is expected that the additives can exist more stably, compared to the case where they are added singly. For these reasons, it is presumed that mechanical strength of the sintered body is
20 greatly improved by synergistic effect between the two additives, compared to the case where they are used singly, whereby the sintered body of aluminum-based titanate having high mechanical strength exceeding practically usable level and very high refractoriness due to greatly
25 enhanced resistance to thermal decomposition is formed

without losing low thermal expansion that is inherent in aluminum titanate.

[0022]

The starting material mixture comprising TiO_2 ,
5 Al_2O_3 , alkali feldspar and Mg-containing component may be uniformly mixed, pulverized to a suitable particle size and then formed into a desired shape.

[0023]

The process of mixing and pulverizing the
10 starting material mixture is not particularly limited, and may be any known process, e.g., mixing and pulverizing by using a ball mill, stirred media mill, etc.

[0024]

The degree of pulverization of the starting
15 material mixture is not critical. Usually, the material is pulverized to a particle size of about 1 μm or less, preferably to as small particle size as possible, as long as secondary particles are not formed.

[0025]

20 A forming aid may further be added to the starting material mixture, if necessary. The forming aid may be selected from substances which have been heretofore used, when required, depending on the forming method.

25 [0026]

Examples of such a forming aid include polyvinyl alcohol, microwax emulsion, carboxymethyl cellulose and like binders, stearic acid emulsion and like mold releasing agents, n-octyl alcohol, octylphenoxy ethanol
5 and like antifoaming agents, diethylamine, triethylamine and like deflocculants, etc.

[0027]

The amount of the forming aid used is not critical, and may be suitably selected within the range
10 of the amount heretofore used for the forming aids depending on the forming method. For example, as a forming aid for slip casting, it is possible to use a binder in an amount of about 0.2 to 0.6 parts by weight, a deflocculant in an amount of about 0.5 to 1.5 parts by
15 weight, a releasing agent (calculated as solids) in an amount of about 0.2 to 0.7 parts by weight, and an antifoaming agent in an amount of about 0.5 to 1.5 parts by weight, per 100 parts by weight the total amount of TiO_2 and Al_2O_3 .

20 [0028]

The method of forming the starting material mixture is not particularly limited and may be suitably selected from known forming methods such as press molding, sheet casting, slip casting, extrusion molding, injection
25 molding, CIP molding, etc.

[0029]

The sintering temperature may be about 1300 to 1700°C, preferably about 1350 to 1450°C.

[0030]

5 The atmosphere for sintering is not particularly limited, and may be any of an oxygen-containing atmosphere such as air, a reducing atmosphere and an inert atmosphere, which are heretofore employed in the prior art.

10 [0031]

 The sintering time is not particularly limited, and may be such that the product is fully sintered depending on the shape of the formed product, etc. Usually, the sintering is conducted for about 1 to 10
15 hours while maintaining the temperature range mentioned above. The heating rate and cooling rate in sintering are not particularly limited, and may be suitably selected so that no cracks are formed in the sintered body.

[0032]

20 The sintered body obtained by the process of the invention has the features as mentioned above; for example, high mechanical strengths and low coefficient of thermal expansion are achieved at the same time. Further, the sintered body has excellent resistance to
25 decomposition due to the stabilized crystal structure,

and a high degree of refractoriness. Accordingly, decomposition reaction of aluminum titanate is inhibited and the product can be stably used even at high temperatures such as a few hundred to about 1600°C. As
5 for bending strength, a very high bending strength of over about 90 MPa, which is about 6 times higher than those of known sintered bodies of aluminum titanate, can be attained. In addition, according to the process of the present invention, sintering without the formation of
10 cracks is possible so that the resulting sintered body becomes closely compacted and has high resistance to thermal shock.

[0033]

The sintered body prepared by the process of the
15 present invention shows very high non-wettability and corrosion resistance against molten metal. As a result, it exhibits such excellent erosion resistance against flow of molten metal that could never be expected for known materials.

20 [0034]

The sintered body of aluminum-based titanate of the invention, utilizing its excellent features mentioned above, can be used for various applications, for example, containers for high-melting point metals such as
25 crucibles for melting metals, ladles and tapping spouts;

components for high-temperature portions of aircraft jet engines; jet nozzles; components for high-temperature portions of various internal combustion engines such as glow plugs, cylinders and piston heads; insulating and
5 shielding plates for outer walls of spacecrafts, etc. Furthermore, it can be effectively used as a surface plate for printing processing in LSI manufacturing processes, etc., utilizing its low expansibility.

[0035]

10 [Effects of the Invention]

As can be seen from the above, the sintered body of aluminum-based titanate obtained by the producing process of the invention has high mechanical strengths and resistance to thermal shock, while maintaining the
15 inherent low expansion coefficient of aluminum titanate. In addition, the sintered body of aluminum-based titanate has excellent resistance to decomposition, exhibits a high value of refractoriness, and can be stably used at high temperatures.

20 [0036]

[Examples]

The present invention is described below in more detail with reference to the following examples.

[0037]

25 Example 1

To 100 parts by weight of a mixture comprising 43.9% by weight (50 mol%) of titanium oxide in anatase form and 56.1% by weight (50 mol%) of sinterable α -alumina were added 4 parts by weight of the alkali feldspar represented by the formula: $(\text{Na}_{0.6}\text{K}_{0.4})\text{AlSi}_3\text{O}_8$, 6 parts by weight of the spinel represented by the formula: MgAl_2O_4 , 0.25 parts by weight of polyvinyl alcohol as a binder, 1 part by weight of diethylamine as a deflocculant and 0.5 parts by weight of polypropylene glycol as an antifoaming agent. The mixture was mixed using a ball mill for 3 hours and then dried using a dryer at 120°C for 12 hours or more, giving a starting material powder.

[0038]

The resulting material powder was pulverized to a particle size passing 150-mesh sieve and pressed under a pressure of 60 MPa, giving a molded product measuring 100 mm × 100 mm × 10 mm.

[0039]

This molded product was sintered according to the heating pattern described below in the atmosphere and thereafter left to cool, giving a sintered body of aluminum-based titanate.

(Heating pattern)

from 0 to 180°C over 6 hours

maintained at 180°C for 4 hours (water
evaporation)

from 180 to 340°C over 4 hours

maintained at 340°C for 4 hours (organic binder
5 combustion)

from 340 to 700°C over 4 hours

maintained at 700°C for 2 hours (residual carbon
combustion)

from 700 to 1400°C over 4 hours

10 maintained at 1400°C for 4 hours

A 5 mm × 5 mm × 20 mm sample was cut from the
resulting sintered body. The surface of the sample was
polished, and the coefficient of thermal expansion of the
15 sample was determined at the heating rate of 20°C/min.
The results are shown in Table 1 below.

[0040]

[Table 1]

Table 1

Temperature (°C)	Percentage of thermal expansion ($\Delta L/L$) %	Average coefficient of thermal expansion ($\times 10^{-7}/K$)
126	-0.016	-15.55
226	-0.029	-14.26
326	-0.036	-12.13
426	-0.040	-10.10
526	-0.039	-7.87
626	-0.033	-5.47
726	-0.014	-2.07
826	0.012	1.55
926	0.035	3.85

5

[0041]

As can be seen from the results shown above, the sintered body obtained by the process of the invention has a low coefficient of thermal expansion and maintains the inherent low thermal expansibility of aluminum titanate.

10

[0042]

Example 2

A sintered body of aluminum-based titanate was

obtained in the same manner as in Example 1 using the same starting material as that used in Example 1 except that the heating pattern in sintering was as described below.

(Heating pattern)

5 from 0 to 180°C over 6 hours

maintained at 180°C for 4 hours (water evaporation)

from 180 to 340°C over 4 hours

10 maintained at 340°C for 4 hours (organic binder combustion)

from 340 to 700°C over 4 hours

maintained at 700°C for 2 hours (residual carbon combustion)

from 700 to 1350°C over 4 hours

15 maintained at 1350°C for 4 hours

A 3 mm × 4 mm × 40 mm sample was cut from the resulting sintered body of aluminum-based titanate. The surface of the sample was polished, and the sample was
20 tested for its three-point bending strength.

[0043]

For comparison, two control examples were prepared: a sintered body (Comparative Example 1) obtained by using the starting material having the same
25 formulation as that used in Example 1 and sintering in

the same manner as in Example 2 (sintering temperature: 1350°C) except that no spinel was used and 4 parts by weight of alkali feldspar was used as an only additive; and a sintered body (Comparative Example 2) obtained by using the starting material having the same formulation as that used in Example 1 described above and sintering under the same conditions as in Example 2 (sintering temperature: 1350°C) except that no alkali feldspar was used and 6 parts by weight of spinel was used as an only additive. These sintered bodies were tested for their three-point bending strength in the same manner. The results are shown in Table 2 below.

[0044]

Table 2

Table 2

Sample name	Three point bending strength (MPa)
Example 2 (feldspar and spinel added)	85.7
Comparative Example 1 (feldspar added)	56.0
Comparative Example 2 (spinel added)	30.3

[0045]

As can be seen from the results shown above, the sintered body of aluminum-based titanate of Example 2 obtained by adding alkali feldspar and spinel at the same

time has higher mechanical strength than the sintered bodies of aluminum-based titanate of Comparative Example 1 and Comparative Example 2 obtained by adding either alkali feldspar or spinel.

5 [0046]

 In addition, a sample measuring 10 mm × 10 mm × 10 mm was cut from each of the sintered bodies of aluminum-based titanate of Example 2, Comparative Example 1 obtained by adding alkali feldspar only and Comparative
10 Example 2 obtained by adding spinel only. The samples were placed in the atmosphere at 1000°C, and the change of the residual aluminum titanate percentage over time was determined by X-ray diffraction method. The residual aluminum titanate percentage was calculated by measuring
15 the diffraction intensity of the (110) and (101) faces of rutile, and determining the amount of rutile from the sum of their areas because aluminum titanate decomposes into alumina and rutile.

 [0047]

20 Further, the sintered body obtained by using the starting material having the same formulation as that used in Example 1 except that neither spinel nor alkali feldspar was added and sintering under the same conditions as in Example 1 (sintering temperature:
25 1400°C) was tested for the change of the residual

aluminum titanate percentage over time in the same manner.
The results are shown as a graph in Fig. 1.

[0048]

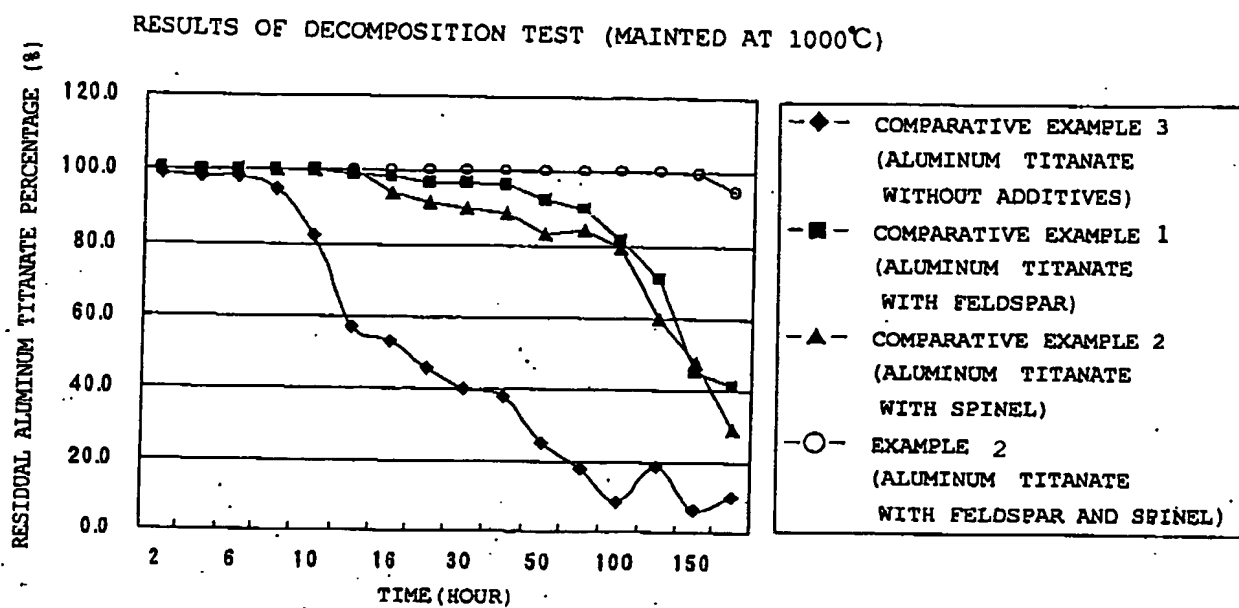
As can be seen from Fig. 1, the sintered body of
5 aluminum-based titanate of Example 2 was hardly
decomposed into TiO_2 and Al_2O_3 when it was left at a high
temperature for a long period. This demonstrates that it
has excellent resistance to thermal decomposition.

[Brief Description of the Drawings]

10 [Fig. 1] Fig. 1 is a graph showing the change of
residual aluminum titanate percentage over time placed in
the atmosphere at 1000°C .

[Document Name] Figure

[Fig. 1]



[Document Name] Abstract

[Abstract]

[Object] An object of the present invention is to provide a sintered body of aluminum-based titanate having an improved mechanical strength and ability to be stably used at high temperatures as well as their inherent properties, i.e., low coefficient of thermal expansion and high corrosion resistance.

[Method for Achieving the Object] A process for preparing a sintered body of aluminum-based titanate, the process comprising sintering a formed product at a temperature of 1300 to 1700°C

the formed product being prepared from a mixed starting material comprising:

100 parts by weight of a mixture comprising 40 to 50 mol% of TiO_2 and 60 to 50 mol% of Al_2O_3 ,

1 to 10 parts by weight of an alkali feldspar represented by the formula: $(\text{Na}_x\text{K}_{1-x})\text{AlSi}_3\text{O}_8$ ($0 \leq x \leq 1$), and

1 to 10 parts by weight of at least one Mg-containing component selected from the group consisting of a Mg-containing oxide with spinel structure, MgCO_3 and MgO .

[Selected Figure] Figure 1



Japanese Patent Office (JP)
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F02F 1/24 C 7616-3G

Examination not requested
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(21) Patent Application No.: H03-65682	Applicant:000125934 ISUZU CERAMICS RESEARCH INSTITUTE Co., Ltd. 8 Tsuchidana, Fujisawa-shi, Kanagawa, Japan
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(54) [Title of the invention]
High strength and low thermal-expansion ceramic

(57) [Abstract]
[Object]

To provide a high strength and low thermal-expansion ceramic.
[Constituents of the invention]

A high strength and low thermal-expansion ceramic is prepared
by adding sumecton SA, which is an inorganic polymer, to aluminum
titanate.

Sample No.	Al ₂ O ₃ 1 TiO ₂ 1	Additive	Binder	Coefficient of thermal expansion ×10 ⁻⁶ /C°	Strength g/mm ²
1	90 wt%	TiO ₂ 5 wt%	Clay A 5 wt%	1.5	3
2	90 wt%	TiO ₂ 5 wt%	Clay B 5 wt%	1.0	2
3 (present invention)	90 wt%	TiO ₂ 5 wt%	Sumecton SA 5 wt%	1.0	3.5
4 (present invention)	90 wt%	TiO ₂ 5 wt%	Sumecton SA 5 wt%	1.3	4.5

[Claims]

[Claim 1] A high strength and low thermal-expansion ceramic, which is characterized by adding, as an additive, sumecton that is an inorganic polymer to aluminum titanate.

5 [Claim 2] The high strength and low thermal-expansion ceramic according to Claim 1, which is characterized by adding, as an additive, sumecton in which sodium ions have been replaced by ammonium ions by ion exchange.

10 [Claim 3] The high strength and low thermal-expansion ceramic according to Claim 1, which is characterized by comprising, in addition to sumecton, at least one member of MgO, ZrO₂, Y₂O₃, SiO₂ and zircon.

[Claim 4] The high strength and low thermal-expansion ceramic according to Claim 1, wherein the content of K₂O as an impurity is not more than 0.01 wt%.

15 [Detailed description of the present invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a high strength and low thermal-expansion ceramic.

20 [0002]

[Prior Art]

Engine parts such as inlet ports, outlet ports, cylinders, pistons and the like are subjected to high temperatures and are required to have a certain degree of strength. Moreover, to attain a certain level of engine performance requires seal against leakage at the inlet port and outlet port and seal between the cylinder and piston and/or between a cylinder liner and cylinder head. In addition, high thermal shock resistance is also important. Thus, materials for parts requiring high temperature resistance and seal as described above must have a low coefficient of thermal expansion.

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[0003]

For example, aluminum titanate can be mentioned as a material having such properties. Aluminum titanate has a high melting point of 1860°C as well as low coefficient of thermal expansion, and thus is suitable for use under high temperature conditions. Aluminum

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titanate, however, is disadvantageous in that its strength is low and it is likely to decompose.

[0004]

Heretofore, in order to improve the disadvantageous properties of aluminum titanate and put it into practical use in mechanical parts such as engines and the like, ZrO_2 , MgO , SiO_2 etc., have been used, in addition to aluminum oxide and titanium oxide, so that decomposition at high temperatures is inhibited, strength is improved, coefficient of thermal expansion is lowered and hysteresis is eliminated. With the addition of such additives, aluminum titanate ensures the adequate physical properties of ceramic. However, forming aluminum titanate into the shape of practically-used parts requires further addition of a binder. Heretofore, a clay having the formulation shown in Fig. 1 has been generally used as a conventionally-used binder.

[0005]

[Problem to be Solved by the Invention]

However, when such a clay is used as a binder in a slip casting method, there are changes in slip properties, mold releasability, drying shrinkage degree and heating shrinkage degree. Moreover, clay is also problematic in accelerating the decomposition of aluminum titanate at high temperatures due to the large amount of Al_2O_3 contained therein. Accordingly, clay poses problems when used for production of precision parts such as outlet ports of engine parts and the like.

[0006]

The present invention was accomplished in view of the drawbacks of the prior art described above. More specifically, the invention provides a high strength and low thermal-expansion ceramic with the use of an inorganic polymer as a binder during preparation of aluminum titanate.

[0007]

[Means for Solving the Problem]

In order to solve the above problems, the invention provides a manner for adding sumecton that is an inorganic polymer as an additive (binder) to aluminum titanate.

[0008]

[Action]

The addition of sumecton that is an inorganic polymer to aluminum titanate can provide a high strength and low thermal-expansion ceramic.

5 [0009]

[Examples]

The following description is given to explain Examples of the invention. Examples used, as a binder, sumecton SA that is a synthetic inorganic polymer (trade name, product of Kunimine Industries Co., Ltd.). Sumecton SA is represented by Formula shown in Fig. 2. The chemical analysis values are as shown Fig. 3. The numerical values in the figures are expressed in wt%. The content of K₂O as an impurity is 0.01 wt% or lower in this sumecton. The examination results are shown in Figs. 4 and 5.

15 [0010]

As is clear from Fig. 4, samples Nos. 3 and 4 prepared using sumecton SA as a binder exhibit higher strength compared to samples Nos. 1 and 2 prepared using conventionally-used binders, although there is no noticeable difference in the coefficients of the thermal expansion therebetween. When this experiment was performed using sumecton SA in which sodium ions were replaced by ammonium ions by ion exchange, the similar results were obtained. Moreover, when this experiment was performed using aluminum titanate further comprising at least one member of MgO, ZrO₂, Y₂O₃, SiO₂ and zircon in addition to sumecton, the similar results were obtained.

[0011]

Subsequently, the inhibitory effect on the decomposition of aluminum titanate maintained at 110°C for 100 hours was measured. The measurement results are shown in Fig. 5. As is clear from Fig. 5, the binder used in the Examples shows an extremely low decomposition level of alumina titanate compared to the conventionally-used binders (samples Nos. 1 and 2). This is because the Al₂O₃ content of the binder used in Examples is smaller than that of the conventionally-used binders and because the composition of the binder is extremely stable due to being a synthetic material. The size of the particles is

submicron and thus the particles are uniformly distributed between the particles of aluminum titanate to effectively functions as a binder and decomposition inhibitor. When the clay is used in a weight of, for example, 5 wt%, the impurity level, i.e., K₂O content, is remarkably
5 reduced, and therefore, the use of clay as a binder possibly improves high temperature properties.

[0012]

[Effect of the Invention]

As described above in detail, the invention has provided a high
10 strength and low thermal expansion ceramic by the addition of sumecton that is an inorganic polymer serving as a binder. Accordingly, the invention achieves an excellent effect that high-precision parts are manufactured.

15 [Brief Descriptions of the Drawings]

[Fig. 1] Fig. 1 shows a clay composition.

[Fig. 2] Fig. 2 shows the chemical formula of sumecton SA.

[Fig. 3] Fig. 3 shows chemical analysis values of sumecton SA.

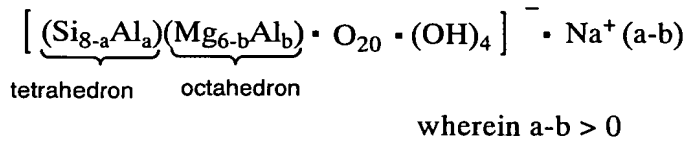
[Fig. 4] Fig. 4 shows comparison results between the invention and
20 prior art.

[Fig. 5] Fig. 5 shows comparison results of the decomposition level of binders of the invention and of the prior art.

[Fig. 1]

Composition of clay	
SiO ₂	49.3 wt%
Al ₂ O ₃	33.5 wt%
Fe ₂ O ₃	1.4 wt%
TiO ₂	0.8 wt%
CaO	0.2 wt%
MgO	0.2 wt%
K ₂ O	0.7 wt%
Na ₂ O	0.1 wt%
Ig Loss	13.8 wt%

[Fig. 2]



[Fig. 3]

SiO ₂	53 wt%
Al ₂ O ₃	5 wt%
MgO	30 wt%
Other ingredients	12 wt%

[Fig. 4]

Sample No.	Al ₂ O ₃ 1 TiO ₂ 1	Additive	Binder	Coefficient of thermal expansion ×10 ⁶ /C°	Strength g/mm ²
1	90 wt%	TiO ₂ 5 wt%	Clay A 5 wt%	1.5	3
2	90 wt%	TiO ₂ 5 wt%	Clay B 5 wt%	1.0	2
3 (present invention)	90 wt%	TiO ₂ 5 wt%	Sumecton SA 5 wt%	1.0	3.5
4 (present invention)	90 wt%	TiO ₂ 5 wt%	Sumecton SA 5 wt%	1.3	4.5

[Fig. 5]

Sample No.	Decomposition level at 1100°C for 100 hours
1	5%
2	7%
3 (present invention)	0.5%
4 (present invention)	0.8%